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SOME RECENT DEVELOPMENTS IN THE CHEMISTRY OF BORON, FLUORINE, AND THEIR COMPOUNDS

[Numbers in parentheses refer to appended list of sources.]

A new method for the quantitative analysis of boron by colorimetric means with carmine indicator is suggested in a recently published paper (1) by Soviet chemists in this field. They also show how to separate boron from fluorine by the use of synthetic resins and have developed a method for the determination of the contents of boron and fluorine in a number of minerals: tourmaline, wiluite, and axinite.

Addition compounds of boron fluoride have become important as catalysts in the fuel industry, and a series of articles on the theme "Compounds of Boron Fluoride as New Catalysts in Alkylation and Polymerization" has appeared in recent issues of Soviet periodicals. The authors are A. V. Topchiyev, newly designated Active Member of the Academy of Sciences USSR (2), and his collaborator, Ya. M. Paushkin.

Reports V and VI of this series (3, 4) are concerned, respectively, with the alkylation of isopentane with propylene and with the alkylation of isopentane with ethylene or isobutylene. Both articles begin with historical reviews of the application of boron fluoride addition compounds as catalysts in this field and point out their increasing importance before going into experimental results. In the introductions to these articles, five references (5-9) are given to previous Soviet research in the field.

Results of two recent investigations (3, 4) by Topchiyev and Paushkin, who employed spectroscopy by the method of light-scattering for analysis of the alkylation products, are as follows:

In connection with the alkylation of isopentane with propylene, they discovered that in reactions of alkylation of isoparaffins with olefins, only compounds of boron fluoride with hydroxyl-containing substances (water, an acid, or an alcohol) are catalytically active. Compounds of these substances with boron fluoride have the character of strong acids and their

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catalytic activity amounts to ordinary acid catalysis. Addition compounds of boron fluoride with simple and complex esters and amines, as well as pure boron fluoride itself, are catalytically inactive in the alkylation of iso-paraffins.

In the alkylation of isopentane with propylene, by using boron fluoride compounds with water and phosphorus pentoxide, the product of alkylation was obtained with a yield of 175-200 percent based on the original propylene or 70-85 percent of the theoretical. Under optimum conditions the product had a specific gravity of D_4^{20} 0.705-0.715, and 70-80 percent of the product boiled away below 170 degrees centigrade.

Topchiyev and Paushkin state that the chemical composition of the products of alkylation depends very little on the catalyst used. Weakly branched hydrocarbons, (2,3-; 2,4- and 2,5-dimethylhexane) are the principal components of the isooctane fraction. On the other hand, in the case of alkylation of isobutane with butylene, the isooctane fraction contains trimethylpentane.

The alkylation of isopentane with propylene gives a product whose octane number is 70.3; the isooctane fraction of the product has a boiling point of 98-120 degrees centigrade and an octane number of 80.6 (that is, a number which is lower than that of the original isopentane which is rated at 89). For this reason, the products of alkylation of isopentane with propylene are not recommended as components of motor fuels in view of their low octane numbers, as compared with products of alkylation of isobutane with olefins.

A number of boron fluoride catalysts were used in the alkylation of isopentane with ethylene and isobutylene, and it was confirmed that only the compounds of boron fluoride with hydroxyl-containing substances, or acid [and acid hydrates] are catalytically active in this reaction, a fact also pointed out by the authors in the previous article.

Acids such as hydrofluoric, sulfuric, and phosphoric do not induce alkylation with ethylene unless they are in combination with boron fluoride.

Alkylation of isopentane with ethylene in the presence of the catalysts phosphorus pentoxide, water, boron fluoride, and $H_2O \cdot BF_3$ proceeds under conditions of atmospheric pressure, although at a slow rate. The yield of the alkylate, in reference to the original ethylene, is 160-200 percent and its specific gravity is 0.69. The alkylation of isopentane with isobutylene proceeds at a greater rate with a yield of 180-220 percent based on the original isobutylene. The alkylate has a specific gravity of 0.71-0.72 and a bromine number of 1-1.5.

The alkylates consist of a mixture of hexanes, heptanes, octanes, and even higher molecular hydrocarbons. The heptane fraction of the products of the alkylation of isopentane with ethylene consist of dimethylpentanes; trimethylbutane is not formed. In the alkylate of isopentane reacted with isobutylene, the nonane fraction composes about 25 percent by weight of the product.

The alkylation of isopentane with ethylene is not of commercial interest because the isopentanes (dimethylpentanes) thus formed have lower octane numbers than the original isopentane. Research on the alkylation of isopentane with ethylene and with isobutylene is significant from the standpoint of the study of activity of individual catalysts.

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Before closing the consideration of the recent work by Topchiyev and Pausshkin, it is interesting to note that they published a monograph, "Properties of Boron Fluoride as a Catalyst in Alkylation, Polymerization, and Condensation" (10), in 1949, and that Topchiyev published another paper, "Nitration of Hydrocarbons and Other Organic Compounds" (10), also in 1949.

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Returning to the paper on the quantitative determination of boron and fluorine (1), a summary of its contents is as follows:

Authors D. I. Ryabchikov and V. V. Danilova of the Institute of Geochemistry and Analytical Chemistry imeni Vernadskiy, Academy of Sciences USSR, state that the determination of boron and fluorine, when both are present, is a very difficult task, and that the determination of small quantities of either is also a challenging proposition. In this investigation, fluorine is determined with zircon alizarin by a previously developed colorimetric method (11); and boron is determined volumetrically by titration of mannitoboric acid with an alkali (12). The latter method is complicated and about 10 percent of the boron escapes detection. Furthermore, commercial mannite almost always contains boron.

The authors (1) recommend their own colorimetric method, in which carmine is used in an indicator in a color action for boron, this having been first suggested by Kazarinova-Oknina (13). In the presence of carmine, a sulfuric acid solution containing boron changes from red to a dark blue. By this method, 0.2 milligram of B_2O_3 in 25 milliliters can be detected. This color and action is interfered with by the presence of oxidizing agents (nitrates, chromates, hydrogen peroxide, etc.) which attack the organic indicator. The presence of fluorine also inhibits the reaction because it and the boron form a complex fluoride which leads to discoloration of the indicator. On the other hand, chlorides do not interfere with the color reaction.

Ryabchikov and Danilova (1) give the following description of their method. A standard solution was prepared from twice recrystallized borax by dissolving it in concentrated sulfuric acid. The original concentration of such a solution was one milligram of B_2O_3 in one milliliter, which was then brought to a lower concentration by dilution (from 0.02 to 0.2 milligram of B_2O_3 in one milliliter). The solution was prepared in 25-milliliter measuring flasks into which, after the introduction of a given portion of the original solution, were added 15 milliliters of the indicator (0.005 percent carmine dissolved in concentrated sulfuric acid). The whole was then diluted up to the mark with concentrated sulfuric acid having a specific gravity of 1.84. After careful mixing and letting the solution stand for an hour, a stable color was observed, and this color was found to persist for not more than 10 days. The addition of water to the solution was avoided, since it changes the color of the indicator.

For the distillation of the boron, Ryabchikov and Danilova used an apparatus which ordinarily serves for the distillation of fluorine. To check the method, a known quantity of boron in solution was put into the apparatus along with 60 millimeters of distilled water and 25 millimeters of concentrated sulfuric acid, in addition to a solution of sodium fluoride in a quantity in excess of that necessary for the formation of boron fluoride. The boron was then distilled from the solution at a temperature of 140 degrees and the combined distillates of three such distillations were found to comprise 200 milliliters.

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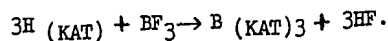
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The remaining water was then distilled off from the sulfuric acid into an Erlenmeyer flask containing 2 milliliters of a one-percent solution of caustic soda by heating the apparatus to the point of formation of vapors of sulfuric acid. The product of this distillation was then added to the first three distillates. The amount of boron remaining in the sulfuric acid was quantitatively determined by colorimetric comparison with standard solutions.

The authors claim that by this method, separation of boron proceeds considerably more rapidly than with methyl alcohol and that it eliminates the loss which occurs in the methyl-alcohol method.

Most of the boron is then contained in the form of boron fluoride in the distillates in which the excess of fluorine is held in the form of sodium fluoride. Determination of boron in the presence of fluorine by ordinary methods is not sufficiently accurate, and that is why the separation of the boron from the fluorine is accomplished with the aid of synthetic resins.

To accomplish this, Ryabchikov and Danilova employed a glass burette with a porous filter. Five to 6 grams of a resin of the type wofatit P pulverized to a grain size of .05 millimeter were placed in the burette. The cationite was treated with dilute hydrochloric acid, 1 to 5, and then was washed with distilled water to the point of a neutral reaction with methyl red. According to the authors, the exchange reaction occurring during the passing of a solution containing boron fluoride through an H-cationite can be designated by the following equation:



The boron in the form of the cation (B^{3+}) was absorbed by the resin and the fluorine anion interacted with the individual hydrogen ions forming hydrogen fluoride and thus passed into the filtrate. The rate of the filtration of the solution through a column with an H-cationite was 50 millimeters per hour. It was necessary to pass the boron fluoride containing solution through the column three or five times. After washing the column with distilled water, the boron was extracted into a separate container with a 2 percent solution of hydrochloric acid (about 200 milliliters) introduced into the column at the original rate, only a small portion of the boron being lost at this rate. Next the column was again washed with distilled water heated to 50 degrees centigrade. The washing water was then added to the main hydrochloric acid filtrate containing boron, and the contents of the measuring flask were brought to the mark.

For the determination of boron, 10 to 20 milliliters of the prepared solution were neutralized with soda in a platinum dish and evaporated to dryness.

Ryabchikov and Danilova (1) give the following table to show the accuracy of the method they recommend, pointing out that the degree of error is decreased when smaller quantities of boron are used:

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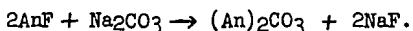
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Boron Used	Fluorine Used	Boron Found in H ₂ SO ₄ Residue	Boron Ex-tracted From Cationite With 2% HCl	Total Boron Found in Experiment	Variance in Theoretical and Experimental Values of Boron	Fluorine in Filtrate After Separation
(in mg)	(in mg)	(in mg)	(in mg)	(in mg)	(in mg) (in %)	(in mg)
0.433	1.2	0.3255	0.0930	0.4185	0.0145	3.35
0.433	1.8	0.3224	0.0992	0.4216	0.0114	2.63
0.345	1.0	0.1302	0.2092	0.3394	0.0066	2.0
0.216	0.65	0.0558	0.1550	0.2108	0.0052	2.40
0.130	0.40	0.0418	0.0860	0.1278	0.0022	1.69
0.087	0.25	0.0471	0.0387	0.0858	0.0012	1.38
						0.24

To check the possibility of a simultaneous determination of fluorine by this method, Ryabchikov and Danilova investigated the remaining filtrate after the separation of the boron. The solution containing hydrogen fluoride was again passed through the column, this time filled with an anionite of the type MGG₁. The degree of pulverization of the resin and the rate at which the solution was passed through the column were the same as in the case of the cationite and the boron determination.

The authors found that the fluorine was completely absorbed by the anionite which had previously been washed with a 4-percent solution of soda, and therefore was in the form (An)₂CO₃. In this case, the reaction can be represented by the equation: (An)₂CO₃ + 2HF → 2AnF + H₂CO₃.

The fluorine was recovered from the anionite by washing the column with a 4-percent solution of soda or caustic soda, which resulted in the formation of sodium fluoride. The column could then be used in subsequent experiments. The regeneration reaction was as follows:



After the column was washed with soda to extract the fluorine from the anionite, the column was again washed with distilled water to attain a neutral reaction. The alkali solution, together with the water used in the washing, was introduced into the apparatus for distillation of the fluorine prior to the determination of the fluorine colorimetrically by the ordinary method with zircon alizarin. Data on the determination of the fluorine are also given in the above table. According to the authors, from the results depicted in the table, it is apparent that the presence of boron does not interfere with the determination of the fluorine.

Therefore, the authors were able to show that, with the aid of ionic exchange resins, it is possible to determine boron and fluorine, when both are present, by the initial separation of the boron. This method has also been tested on the following minerals (14, 15):

Tourmaline--(Na,Ca)R₃B₃Si₁₆O₂₇(OH,F)
 Wiluite--(Ca,Mn,Mg,Fe)O₃Al₂B₂(OH,F)
 Axalite--6(Ca,Fe,Mn)·2Al₂O₃·8SiO₂·H₂O

These minerals were obtained from the Mineralogical Museum of the Academy of Sciences USSR. In each case about 0.02-0.1 gram of the pulverized mineral was mixed with soda, and the mixture was then lixiviated with water and introduced into the apparatus for distillation. The solution was carefully neutralized and then 25 milliliters of concentrated sulfuric acid with a specific gravity of 1.84 were added, and the distillation of the boron fluoride carried out.

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Contents of B_2O_3 and F in mineral specimen were as follows:

First specimen of wiluite--4.66% of B_2O_3 , 0.24% of F
 Second specimen of wiluite--4.64% of B_2O_3 , 0.26% of F
 First specimen of tourmaline--7.53% of B_2O_3 , 0.37% of F
 Second specimen of tourmaline--7.59% of B_2O_3 , 0.38% of F
 First specimen of axalite--4.66% of B_2O_3 , no F

To check results, the authors used a known quantity of boron and fluorine in one of the parallel tests on the mineral specimens. The known quantities were then compared with the experimentally obtained quantities for each element.

Ryabchikov and Danilova submitted their article 5 November 1949. The articles by Topchiyev and Paushkin were submitted 24 June 1948. Other researchers at the Ural Scientific-Research Chemical Institute at Sverdlovsk and the Laboratory of General Chemistry at Dnepropetrovsk Metallurgical Institute are known to be working on complementary problems connected with compounds of boron and fluorine (16, 17)

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